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Applicant: IBIDEN CO LTD

[Title Of The Invention]

SOLDER RESIST COMPOSITION AND PRINTED WIRING BOARD

[Abstract]

PROBLEM TO BE SOLVED: To make easy the application of a solder resist composition by a roll coater and reduce the migration of lead from it, by making it contain both the acrylate of a novolak type epoxy resin and an imidazole hardening agent, and by adjusting its viscosity to a specific scope at a specific temperature, using a glycolic ether-based solvent.

SOLUTION: A solder resist composition contains both the acrylate of the novolak type epoxy resin obtained by the reaction of the glycidyl ether of either phenol novolak or crezol novolak on either acrylic acid or methacrylic acid and such a liquid imidazole hardening agent as 1-benzyl-2-methylimidazole, 1-cyanoethyl-2-ethyl-4-methylimidazole, and 4-methyl-2-ethylimidazole. Further, its viscosity is adjusted to 0.5-10 Pa.s at 25°C, using a kind of glycol ether-based solvent selected for diethylene glycol dimethyl ether and triethylene glycol dimethyl ether.

[Claim(s)]

[Claim 1] A soldering resist composition which adjusts viscosity to 0.5-10 Pa and, and s at 25 degrees C using a glycol ether system solvent including acrylate and an imidazole hardening agent of novolak type epoxy resin.

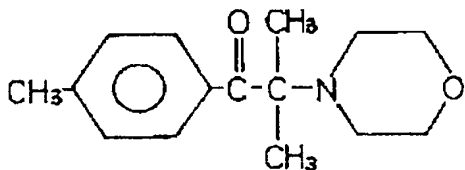
[Claim 2] A soldering resist composition containing acrylate of novolak type epoxy resin, an imidazole hardening agent, and a polymer of acrylic ester.

[Claim 3] A soldering resist composition which adjusts viscosity to 0.5 - 10 Pa-s at 25 degrees C using a glycol ether system solvent including acrylate of novolak type epoxy resin, an imidazole hardening agent, and a polymer of acrylic ester.

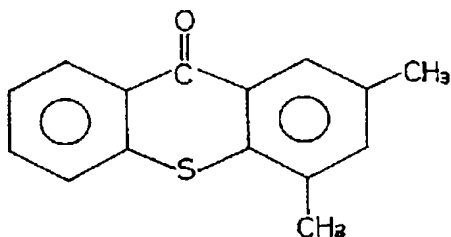
[Claim 4] The soldering resist composition according to claim 2 or 3 which a polymer of said acrylic ester is molecular weight 500-5000, and is a polymer of ester of acrylic acid or methacrylic acid, and alcohol of the carbon numbers 1-10.

[Claim 5] Claims 1-3 containing a compound which has the structure of the following chemical formula 2 as a photosensitizer as an initiator including a compound with structure of the following chemical formula 1 are not, but it is a soldering resist composition.

[Formula 1]



[Formula 2]



[Claim 6] Liquefied claims 1-3 are not at a room temperature, but said imidazole hardening agent is a soldering resist composition.

[Claim 7] In a printed wired board which it has, a solder resist layer on the surface of a wiring board in which a conductor circuit was formed said solder resist layer, A printed wired board which stiffens a soldering resist composition which adjusted viscosity to 0.5 - 10 Pa-s at 25 degrees C using a glycol ether system solvent including acrylate and an imidazole hardening agent of novolak type epoxy resin, forms, and is characterized by things.

[Claim 8] Said a part of conductor circuit exposed from an opening which a solder resist layer was provided in that surface, and was provided in this solder resist layer is formed as a pad to a wiring board in which a conductor circuit was formed, A printed wired board, wherein said solder resist layer contains acrylate and an imidazole hardening agent of novolak type epoxy resin in a printed wired board which carries out supply maintenance of the solder object on the pad.

[Claim 9] The printed wired board according to claim 7 or 8, wherein said solder resist layer contains a polymer of acrylic ester.

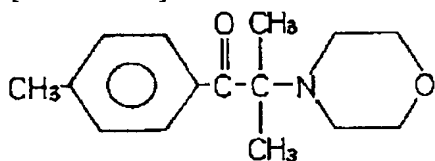
[Claim 10] The printed wired board according to claim 9 which a polymer of said acrylic ester is molecular weight 500-5000, and is a polymer of ester of acrylic acid or methacrylic acid, and alcohol of the carbon numbers 1-10.

[Claim 11] A printed wired board given in any 1 paragraph of claims 7-9 characterized by comprising the following.

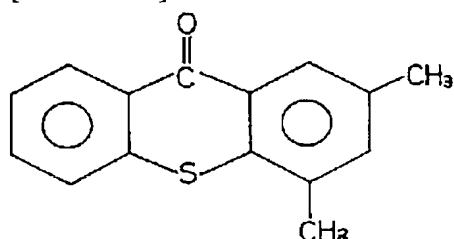
An initiator in which said solder resist layer has the structure of the following chemical formula 3.

A photosensitizer with structure of the following chemical formula 4.

[Formula 3]



[Formula 4]



[Claim 12] The printed wired board according to claim 7 or 8 which comes to form a

roughened layer in the surface of said conductor circuit.

[Claim 13]The printed wired board according to claim 12 which is an alloy layer which said roughened layer turns into from copper-nickel phosphorus.

[Detailed Description of the Invention]

[0001]

[Field of the Invention]About a soldering resist composition and a printed wired board, it is easy to apply especially this invention by a roll coater, and it is proposed about the printed wired board using a leaden soldering resist composition with little migration and this soldering resist composition.

[0002]

[Description of the Prior Art]As for the printed wired board, the solder resist layer is formed in the outermost layer part. This solder resist layer has a function which protects the conductor circuit exposed to the surface, and a function as a dam which prevents a solder outflow and solder bridge of the solder object (for example, solder vamp) supplied to the pad surface in which electronic parts are carried.

[0003]As a resin composition for forming such a solder resist layer, . As [indicate / for example, / by the JP,63-286841,A (USP No. 4902726) gazette] Epoxy acrylate and an imidazole hardening agent are dissolved in a cellosolve acetate, and the soldering resist composition etc. which adjusted the viscosity to 0.1 - 0.2 Pa-s are used. The alkaline development type soldering resist composition is indicated by JP,62-23036,A.

[0004]

[Problem(s) to be Solved by the Invention]However, if the resin composition of a statement is used for JP,63-286841,A as a solder resist layer, The lead ion diffused the inside of a solder resist layer from the solder objects (solder vamp etc.) formed on a pad (this phenomenon is called leaden migration), the flow between pads was caused, and there was a problem of causing a short circuit. Also when the resin composition of a statement was used for JP,62-23036,A as a solder resist layer, the above-mentioned phenomenon was caused too and there was a problem of causing a short circuit.

[0005]On the other hand, when the above-mentioned resin composition was applied to the copper pattern and this was dried, the copper pattern under such a resin layer oxidized, when it gave nickel gilding, the oxidizing zone of this copper pattern dissolved it, and there was a problem that the discoloration called what is called a halo phenomenon occurred.

[0006]When the above-mentioned resin composition was used as a solder resist layer, such a solder resist layer had the problem of being easy to produce exfoliation by a thermo cycle.

[0007]The double-sided wiring board of a printed wired board is basic specification, and a soldering resist composition must be applied to both sides in this case. Therefore, as the best spreading gestalt, where a wiring board is stood vertically, it inserts between the rolls of the roll for spreading of the couple of a roll coater, and there is the method of applying a soldering resist composition to both sides of the substrate simultaneously. However, when this method was adopted, there was a problem of the above-mentioned soldering resist composition concerning conventional technology having too low viscosity, and hanging down.

[0008]This invention is made in order to solve the various problems which conventional

technology has and which were mentioned above, and it is easy to apply the main purpose by a roll coater, and there is leaden migration in developing few soldering resist compositions. Other purposes of this invention are to provide a printed wired board without exfoliation of the solder resist layer by the halo phenomenon or a thermo cycle.

[0009]

[Means for Solving the Problem]Artificers acquired knowledge which is expressed below, as a result of inquiring wholeheartedly towards realization of the above-mentioned purpose. That is, even if viscosity is low (0.1 - 0.2 Pa-s), a crevice exists between chains, and a resin composition given in above-mentioned JP,63-286841,A dries this and carries out exposure hardening, a curing rate is low, and this crevice remains. Therefore, it is thought that a lead ion will move this crevice.

[0010]In order to cut a chain chemically in a resin composition given in JP,62-23036,A having introduced carboxylic acid into an epoxy group, and carrying out alkaline development, it is ruined and it is thought that a lead ion will be spread from this devastated field.

[0011]Since -COOR decomposes and the above-mentioned resin composition which contains a cellosolve acetate as a solvent produces free oxygen (O), it is considered that this is oxidizing a copper surface.

[0012]This invention is developed based on such knowledge, and the gist composition is as follows.

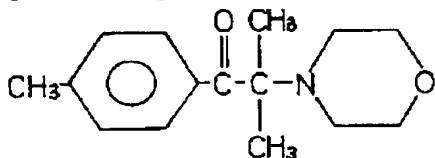
(1) It is a soldering resist composition which adjusts viscosity to 0.5 - 10 Pa-s at 25 degrees C using a glycol ether system solvent including acrylate and an imidazole hardening agent of novolak type epoxy resin.

(2) It is a soldering resist composition containing acrylate of novolak type epoxy resin, an imidazole hardening agent, and a polymer of acrylic ester.

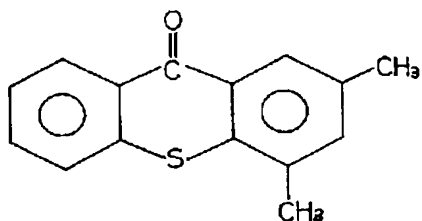
(3) It is a soldering resist composition which adjusts viscosity to 0.5 - 10 Pa-s at 25 degrees C using a glycol ether system solvent including acrylate of novolak type epoxy resin, an imidazole hardening agent, and a polymer of acrylic ester.

[0013]In a soldering resist composition given in above-mentioned (2) or (3), a polymer of acrylic ester is molecular weight 500-5000, and it is preferred that it is a polymer of ester of acrylic acid or methacrylic acid, and alcohol of the carbon numbers 1-10. As for a soldering resist composition given in above-mentioned (1) - (3), it is preferred that a compound with structure of the following chemical formula 6 is included as a photosensitizer as an initiator including a compound with structure of the following chemical formula 5.

[Formula 5]



[Formula 6]



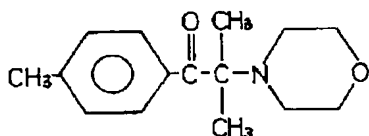
As for said imidazole hardening agent, in a soldering resist composition given in above-mentioned (1) - (3), it is preferred that it is liquefied at 25 degrees C.

[0014](4) In the printed wired board which it has, a solder resist layer on the surface of the wiring board in which the conductor circuit was formed said solder resist layer, It is a printed wired board which stiffens the soldering resist composition which adjusted viscosity to 0.5 - 10 Pa-s at 25 degrees C using the glycol ether system solvent including the acrylate and the imidazole hardening agent of novolak type epoxy resin, forms, and is characterized by things.

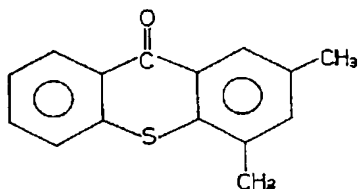
(5) Said a part of conductor circuit exposed from the opening which the solder resist layer was provided in that surface, and was provided in this solder resist layer is formed as a pad to the wiring board in which the conductor circuit was formed, In the printed wired board which carries out supply maintenance of the solder object on the pad, said solder resist layer is a printed wired board becoming considering the acrylate and the imidazole hardening agent of novolak type epoxy resin as the main ingredients.

[0015]In a printed wired board of a statement, to the above (4) or (5), said solder resist layer, It is preferred a polymer of acrylic ester and that are molecular weight 500-5000 more preferably and a polymer of ester of acrylic acid or methacrylic acid, and alcohol of the carbon numbers 1-10 is included. As for said solder resist layer, in a printed wired board the above (4) or given in (5), it is preferred that an initiator with structure of the following chemical formula 7 and a photosensitizer with structure of the following chemical formula 8 are included.

[Formula 7]



[Formula 8]



In a printed wired board the above (4) or given in (5), it is preferred to come to form a roughened layer in the surface of said conductor circuit, and, as for the roughened layer, it is desirable that it is an alloy layer which consists of copper-nickel phosphorus.

[0016]

[Embodiment of the Invention]The soldering resist composition of this invention has the feature of 1 in the point which is a resin composition which uses the acrylate and the imidazole hardening agent of novolak type epoxy resin as the main ingredients. So, the

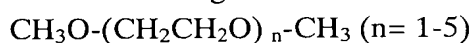
solder resist layer which hardened this resin composition is excellent in heat resistance and alkali resistance, and does not deteriorate at the temperature (around 200 degrees C) which solder fuses, either, and plating liquid like nickel-plating metallurgy plating does not decompose it. Since solvent development is possible for the above-mentioned soldering resist composition, its development side is not ruined like alkaline development.

[0017]a glycol ether system solvent is used for the soldering resist composition of this invention as a solvent -- the viscosity -- 25 degrees C [] -- other features are that it made it into 2 - 3Ps a and s more preferably 0.5 to 10 Pa-s. Thus, the solder resist layer which is obtained according to the soldering resist composition adjusted to the viscosity more than 0.5 Pa and, and s at 25 degrees C, The crevice between resin chain comrades is small, and as a result of diffusion (lead migration) of Pb which moves this crevice decreasing, the short defect of a printed wired board is reduced. If the viscosity of the above-mentioned soldering resist composition is more than 0.5 Pa-s at 25 degrees C, where a substrate is stood vertically, even if it applies to double-sided coincidence, the constituent will not hang down, and good spreading will be attained. However, since spreading by a roll coater was not completed when the viscosity of the above-mentioned soldering resist composition exceeded 10 Pa-s at 25 degrees C, the maximum was made into 10 Pa-s.

[0018]Here, as acrylate of the above-mentioned novolak type epoxy resin, the epoxy resin etc. which made glycidyl ether of phenol novolac or cresolnovolak react to acrylic acid, methacrylic acid, etc. can be used.

[0019]Although various things can be used for the above-mentioned imidazole hardening agent, its liquefied thing is desirable at 25 degrees C. It is because uniform kneading is difficult and the more liquefied one can knead uniformly with powder. As such a liquefied imidazole hardening agent, 1-benzyl- 2-methylimidazole (name of article: 1 B-2 MZ), 1-cyanoethyl- 2-ethyl- 4-methyl imidazole (name of article: 2E4 MZ-CN) and 4-methyl- 2-ethylimidazole (name of article: 2E4MZ) can be used. As for the addition of this imidazole hardening agent, it is desirable to consider it as 1 to 10 % of the weight to the total solid content of the above-mentioned soldering resist composition. This is because it will be easy to mix homogenously if an addition is this within the limits.

[0020]Since the glycol ether system solvent is being used for the above-mentioned soldering resist composition as a solvent, it is not generated by free oxygen and the solder resist layer using such a constituent does not oxidize a copper pad surface. There is also little hazardous property over a human body. as such a glycol ether system solvent -- the thing of the following structural formula -- it is especially chosen out of diethylene glycol dimethyl ether (DMDG) and triethylene glycol wood ether (DMTG) desirably -- one sort is used even if small [either]. These solvents are because the benzophenone and the Michler's ketone which are reactional initiators can be thoroughly dissolved by warming at about 30-50 degrees C.



10 - 40wt% of this glycol ether system solvent is good to the full weight of a soldering resist composition.

[0021]In addition to this in a soldering resist composition which was explained above, a photosensitive monomer etc. can be added for thermosetting resin and a resolution improvement for various defoaming agents, a leveling agent, heat resistance, the improvement of basicity-proof, and flexible grant. Coloring matter and paints may be added to a soldering resist composition. It is because a circuit pattern can be concealed. It

is desirable to use Phthalocyanine Green as this coloring matter.

[0022]In particular, at this invention, it is a molecular weight in a soldering resist composition. It is desirable to add the polymer of about 500 to 5000 acrylic ester. It is because this polymer is liquefied at 25 degrees C, and it is easy to dissolve with cresol-novolak-epoxy-resin acrylate and has a leveling operation and a defoaming operation. For this reason, the formed solder resist layer is excellent in surface smoothness, and does not have unevenness by crawling or air bubbles, either. Since this polymer has compatibility with a photosensitive resin component, distributes it in a resinous principle and translucency is not reduced, it is hard to generate the development remainder.

[0023]As for the polymer of acrylic ester used for this invention, it is desirable that it is a polymer of ester with alcohol of the carbon numbers 1-10 and acrylic acid, methacrylic acid, or its derivative. the carbon numbers 1-10 used for this invention -- as alcohol of the carbon numbers 3-8 preferably, Propyl alcohol, isopropyl alcohol, n-butyl alcohol, Polyhydric alcohol, such as monohydric alcohol, such as tert-butyl alcohol, isobutyl alcohol, pentyl alcohol, hexyl alcohol, octyl alcohol, 2-ethylhexyl alcohol, and amyl alcohol, and 1,2-ethanediol, etc. are mentioned.

[0024]The polymer of this acrylic ester is excellent in compatibility with cresol-novolak-epoxy-resin acrylate, in particular, it is chosen out of 2-ethylhexyl acrylate (2EHA), butyl acrylate (BA), ethyl acrylate (EA), and hydroxyethyl acrylate (HEA) -- even if small [either], the polymer of one or more sorts of acrylic ester is desirable. Since 2-ethylhexyl acrylate has branched, it can give a surface activity operation, and it prevents plating resist from being flipped by garbage etc. Butyl acrylate bears a leveling operation and a defoaming operation, and it is thought that ethyl acrylate and hydroxyethyl acrylate raise compatibility. said four sorts of acrylate is independent in that to which copolymerization of two or more sorts of acrylate which is independent, uses two or more sorts together, or is chosen from said four sorts of acrylate was carried out for what was polymerized independently, respectively -- or it may be mixed and used.

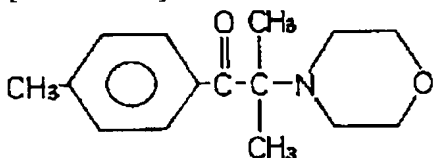
[0025]For example, when using all of said four sorts of acrylate, those weight composition ratios, As for 2-ethylhexyl acrylate/butyl acrylate, 40 / 60 - 60/40 are desirable, As for the mixture / hydroxyethyl acrylate of 90 / 10 - 97/3, 2-ethylhexyl acrylate, and butyl acrylate, 95 / 5 - 99/1 are [the mixture/ethyl acrylate of 2-ethylhexyl acrylate and butyl acrylate] desirable.

[0026]Molecular weight of the polymer of such acrylic ester 500 to about 5000 are preferred. In this range, in 25 degrees C, it is liquefied, and when preparing a solder resist, it is easy to mix with a photopolymer. If a molecular weight exceeds 5000, viscosity will become high and a leveling operation and a defoaming operation will fall. Conversely, a molecular weight. Neither a leveling operation nor a defoaming operation is seen by less than 500. Especially the molecular weights of the desirable polymer of acrylic ester are 2000-3000. In this range, viscosity serves as 250 - 550cp (25 degrees C), and it becomes further easy to prepare a solder resist.

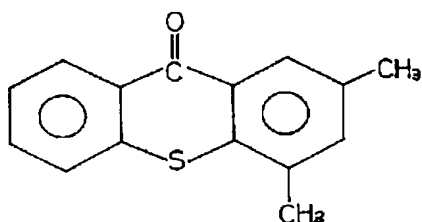
[0027]The addition of the polymer of acrylic ester is 0.2-1.0 preferably 0.1 to 5 weight section to photosensitive resin component 100 weight section. It is desirable to consider it as a weight section. It is because a leveling operation and a defoaming operation fall that they are less than 0.1 weight sections, a glass transition point will fall and heat resistance will fall, if it is easy to generate Pb migration and the crack resulting from air bubbles and five weight sections are exceeded conversely.

[0028] It is desirable to add the compound which has the structure of the following chemical formula 9 in a soldering resist composition as an initiator, and which has the structure of the following chemical formula 10 as a photosensitizer in this invention. It is because these compounds are easy to come to hand and their safety to a human body is also high.

[Formula 9]



[Formula 10]

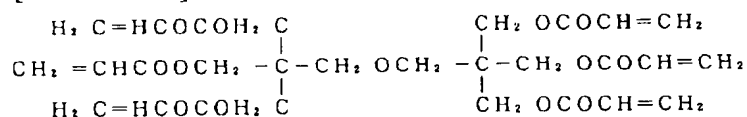


[0029] Bisphenol type epoxy resin can be used as the above-mentioned thermosetting resin quoted as an addition ingredient. The latter is good, when there are a bisphenol A type epoxy resin and an epoxy resin of a bisphenol female mold in this bisphenol type epoxy resin, it thinks basicity-proof as important and hypoviscosity-ization is required for the former (when thinking spreading nature as important).

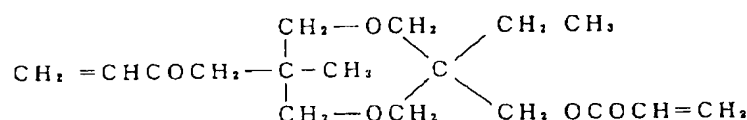
[0030] A multivalent acrylic system monomer can be used as the above-mentioned photosensitive monomer quoted as an addition ingredient. It is because the multivalent acrylic system monomer can raise resolution. For example, the multivalent acrylic system monomer of structure as shown in the following chemical formula 11 and the chemical formula 12 is desirable. Here, the chemical formula 11 is Nippon Kayaku DPE-6A, and the chemical formula 12 is R-604 made from the Kyoeisha chemicals.

[0031]

[Formula 11]



[Formula 12]



[0032] Benzophenone (BP) and a Michler's ketone (MK) may be added to a soldering resist composition. It is because these act as an initiator and a reaction accelerator. As for this BP and MK, it is desirable to make it dissolve in the glycol ether system solvent heated at 30-70 degrees C simultaneously, to mix homogenously, and to mix with other ingredients. It is because there is no dissolution residue and it can dissolve thoroughly.

[0033] In the printed wired board which has a solder resist layer on the surface of the

wiring board in which the conductor circuit was formed, the printed wired board of this invention stiffened the soldering resist composition concerning this invention which mentioned said solder resist layer above, and was constituted. That is, said solder resist layer is characterized by being a hardened material of the resin composition which uses the acrylate and the imidazole hardening agent of novolak type epoxy resin as the main ingredients.

[0034]In a printed wired board of this invention, a wiring board, Although not limited in particular, it is desirable that it is what is called an additive printed wired board and a build up multilayer printed wiring board with which plating resist was formed on resin insulation with which roughening treatment of the surface was carried out, and a conductor circuit which contains a pad in an agenesys portion of the plating resist was formed. When applying a soldering resist composition to such a wiring board, an opening diameter of a solder resist layer can be made larger than a diameter of contact pads. Thereby, with a solder object, plating resist which is resin acts as a dam of a solder object in order to flip this solder object, without getting used. It is also possible to make an opening diameter of a solder resist layer smaller than a path of a pad, and to cover a part of pad with a solder resist layer conversely. In this case, a roughened layer of a pad can eat into a solder resist, a solder resist layer and a pad can stick, and exfoliation of a pad can be controlled.

[0035]As for solder resist layer thickness, in a printed wired board of this invention, it is desirable to be referred to as 5-30 micrometers. It is because it will be hard to carry out a development if too thick [if too thin, an effect as a dam of a solder object will fall, and].

[0036]Still more suitable composition as a printed wired board of this invention, As opposed to a wiring board which formed a conductor circuit as shown in drawing 3 and drawing 24, In a printed wired board which a solder resist layer is provided in that surface, and forms as a pad said a part of conductor circuit exposed from an opening provided in this solder resist layer, and carries out supply maintenance of the solder object on that pad, Stiffened a soldering resist composition applied to this invention in said solder resist layer, and it constitutes, and is the structure where a roughened layer is formed in the surface of said conductor circuit. In a printed wired board of such a structure, since a roughened layer formed in the surface of a conductor circuit containing a pad (portion in which an IC chip and electronic parts are carried) acts as an anchor, a conductor circuit and a solder resist layer have stuck firmly. The adhesion of a solder object by which supply maintenance is carried out is also improved in a pad surface. Since especially acrylate of novolak type epoxy resin has an upright skeleton, it excels in heat resistance and basicity-proof, but since flexibility is missing, it is easy to produce exfoliation under an elevated temperature and humid conditions. According to the above-mentioned composition in which a roughened layer was formed on the surface of this point and a conductor circuit, such exfoliation can be prevented.

[0037]Here, as for the above-mentioned roughened layer, it is desirable to be formed by either grinding treatment, an etching process, an oxidation reduction process and plating processing. An oxidation reduction process among these processings NaOH (10 g/l), NaClO₂ (40 g/l), Na₃PO₄ (6 g/l), using an oxidation bath (melanism bath), NaOH (10 g/l), and NaBH₄ (5 g/l) as a reduction bath plating processing, 8 g/l of copper sulfate, nickel sulfate 0.6 g/l, 15 g/l of citrate, 29 g/l of sodium hypophosphite, 31 g/l of boric acid, and surface-active agent It is desirable to use a nonelectrolytic plating bath for copper-nickel phosphorus plating of pH=9 which consists of 0.1 g/l. It is because it is [especially a

roughened layer of an alloy layer by copper-nickel phosphorus plating] hard in a solder resist layer with needlelike structure, so it contributes to improvement in adhesion with a solder resist layer according to the anchor effect. Since it is electric conductivity, even if it forms a solder object in a pad surface, it is not necessary to remove this roughened layer. [0038]Presentations of an alloy layer which constitutes said roughened layer are copper, nickel, and a rate of Lynn, and it is desirable respectively that it is 0.5 - 2wt% 1 - 5wt% 90 - 96wt%. It is because it has a needlelike structure at the time of these presentation rates. As for thickness of said roughened layer, it is desirable that it is 0.5-7 micrometers. It is because adhesion with a solder resist layer or a solder object falls even if too thick and too thin.

[0039]When carrying out supply maintenance of the solder object on a pad, it is good for the pad surface to give nickel gilding. It is because a nickel layer improves adhesion with copper, and is excellent also in adhesion with gold and familiarity of a gold layer by a solder object is good. A solder object may be stratified and may be what is called a "solder vamp" of ball state.

[0040]Next, law is explained while manufacturing a printed wired board concerning this invention.

(1) Produce first a wiring board in which an inner layer copper pattern was formed on the surface of a core substrate. . [whether formation of a copper pattern to this core substrate is performed by etching copper clad laminate, and] Or an adhesives layer for nonelectrolytic plating is formed in substrates, such as a glass epoxy board, a polyimide substrate, a ceramic substrate, and a metal substrate, and this adhesive layer surface is roughened, it is considered as a roughened surface, and there is a method of performing nonelectrolytic plating here and performing it here. Furthermore, an adhesives layer for nonelectrolytic plating can be formed in the above-mentioned wiring board, an opening for viaholes can be provided in this layer if needed, that layer surface can be roughened, and it can be considered as a wiring board which repeated a process of performing nonelectrolytic plating here and forming a copper pattern and a viahole in it, and was multilayered. A through hole is formed in a core substrate and a wiring layer of the surface and a rear face can electrically be connected to it via this through hole.

[0041](2) Next, form a resin insulation layer between layers on a wiring board produced by the aforementioned (1). It is desirable to use adhesives for nonelectrolytic plating mentioned [especially] above as resin insulation between layers in this invention. These adhesives for nonelectrolytic plating have optimal thing which acid or an oxidizer by which curing treatment was carried out comes to distribute in heat resistant resin whose heat resistant resin particle of fusibility is not hardened [poorly soluble] to acid or an oxidizer. In the above-mentioned adhesives for nonelectrolytic plating, as said heat resistant resin particle by which especially curing treatment was carried out, Floc which mean particle diameter condenses heat resistant resin powder of 10 micrometers or less, and mean particle diameter made condense heat resistant resin powder of 2 micrometers or less, In mean particle diameter, heat-resistant powdered resin powder and mean particle diameter of 10 micrometers or less. A mixture with heat resistant resin powder of 2 micrometers or less, False particles to which one sort is made to come to adhere even if the surface of heat resistant resin powder whose mean particle diameter is 2-10 micrometers has little mean particle diameter either as for heat resistant resin powder of 2 micrometers or less or inorganic powder, ** mean particle diameter 0.1 - a heat resistant resin particle

of 0.8 μm and mean particle diameter -- exceeding 0.8 micrometer -- a mixture with a heat resistant resin particle with a mean particle diameter of less than 2 micrometers, and even if small [either], it is desirable to use one sort. [] It is because these can form a more complicated anchor.

[0042](3) Provide an opening for viahole formation if needed after drying an adhesives layer for nonelectrolytic plating formed above (2). heat-hardening, after exposing in the case of a photopolymer and developing negatives -- in the case of thermosetting resin, an opening for viahole formation is provided in said adhesives layer by [which heat-hardened] carrying out after laser processing.

[0043](4) Next, carry out dissolution removal of the epoxy resin particle which exists in the surface of said hardened adhesives layer with acid or an oxidizer, and carry out roughening treatment of the adhesive layer surface. Here, although there is organic acid, such as phosphoric acid, chloride, sulfuric acid or formic acid, and acetic acid, as the above-mentioned acid, it is desirable to use especially organic acid. It is because it is hard to make a metallic conductor layer exposed from a viahole corrode when roughening treatment is carried out. On the other hand, it is desirable to use chromic acid and permanganates (potassium permanganate etc.) as the above-mentioned oxidizer.

[0044](5) Next, give a catalyst core to a wiring board which roughened an adhesive layer surface. It is desirable to grant of a catalyst core to use precious-metals ion, noble metal colloid, etc., and, generally, it uses a palladium chloride and palladium colloid for it. Heat-treating, since a catalyst core is fixed is desirable. As such a catalyst core, palladium is good.

[0045](6) Next, form plating resist in a wiring board which gave a catalyst core. Although it is desirable to use a constituent which consists of acrylate and an imidazole hardening agent of cresolnovolak or phenol novolak type epoxy resin especially as a plating-resist constituent, a commercial item can also be used for others.

[0046](7) Next, perform nonelectrolytic plating to a plating-resist agenesis part, form a conductor circuit containing a pad and a viahole, and manufacture a printed wired board. Here, as the above-mentioned nonelectrolytic plating, it is desirable to use copper plating.

[0047](8) Next, form a roughened layer on the surface of a conductor circuit if needed. When forming a roughened layer by a copper-nickel phosphorus alloy layer here, this alloy layer is deposited with nonelectrolytic plating. As nonelectrolytic plating of this alloy, 1-40 g/l of copper sulfate, nickel sulfate 0.1 - 6.0 g/l, It is desirable to use a plating bath of liquid composition which consists of 10-20 g/l of citrate, the hypophosphite 10 - 100 g/l, 10-40 g/l of boric acid, and 0.01-10 g/l of surface-active agents.

[0048](9) Next, apply a soldering resist composition concerning this invention to both sides of a printed wired board which finished processing of the above (8). As this invention especially shows to drawing 2, when applying a solder resist layer to both sides of a printed wired board, It is desirable to insert between rolls of a roll for spreading of a couple of a roll coater, where said printed wired board is stood vertically, to make it convey from the bottom to the upper part, and to apply a soldering resist composition to both sides of a substrate simultaneously. Basic specifications of the present printed wired board are both sides, and this is because only one side can be applied in the curtain coat method (how to pour resin from a top to the bottom like a waterfall, make a "curtain" of this resin pass through a substrate, and apply). A soldering resist composition of this invention mentioned above can be used advantageous because of a described method

applied to double-sided coincidence. That is, since viscosity is 1 - 10 Pa-s at 25 degrees C, even if a substrate is stood vertically and a soldering resist composition of this invention applies it, it does not flow, and its transfer is also good.

[0049](10) Next, dry a coat of a soldering resist composition for 5 to 60 minutes at 60-80 degrees C, and form an opening which laid a photomask film which drew an opening in this coat, and exposed a pad portion to it among conductor circuits exposure and by carrying out a development. Thus, a coat in which an opening was formed is stiffened by heat treatment of 1 to 10 hours by 80 more - 150 degrees C. Thereby, a solder resist layer which has an opening sticks with a roughened layer provided on the surface of a conductor circuit. Here, an opening diameter of said opening is made larger than a path of a pad, and it can be carried out to such an extent that a pad is exposed thoroughly. In this case, since a pad is not covered with a solder resist, and a solder resist does not contact a solder object and vena contracta does not arise on a solder object even if a photo mask shifts, on a solder object, it becomes difficult to generate a crack. It is also possible to make an opening diameter of a solder resist layer smaller than a path of a pad, and to cover a part of pad with a solder resist layer conversely. In this case, a roughened layer of a pad can eat into a solder resist, a solder resist layer and a pad can stick, and exfoliation of a pad can be controlled.

[0050](11) Next, give nickel plating and gilding on said pad section exposed from said opening. It is publicly known, for example, concrete plating liquid composition of nickel-plating metallurgy plating is the Maki Shoten Publishing issue and Tokuzo Kobe. It is explained by work, "NP series nonelectrolytic plating" (September 30, 1990 issue), etc. in full detail.

[0051](12) Next, supply a solder object on said pad section exposed from said opening. A solder replica method and print processes can be used as a feeding method of a solder object. A solder replica method pastes solder foil together to prepreg, by leaving and etching only a part which is equivalent to the opening part in this solder foil, forms a solder pattern and uses it as a solder carrier film here, It is the method of laminating this solder carrier film so that a solder pattern may contact a pad, after applying flux to the solder resist opening part of a substrate, and heating and transferring this. On the other hand, print processes are methods of laying a metal mask which provided a breakthrough in a part equivalent to a pad in a substrate, and printing and heat-treating soldering paste.

[0052]A method mentioned above is a manufacturing method of a printed wired board called what is called a fully-additive process, and a method called a semiadditive process besides this method can be used for it. For example, a printed wired board can be manufactured by following methods.

(1) Form an electroless plating film in the whole surface to a substrate which finished a process (5) in a method mentioned above. As this electroless plating film, a non-electrolytic copper plating film is good, and, as for that thickness, 1-5 micrometers is good. This is because a non-electrolytic copper plating film functions as a plating bar and it is easy to remove by etching.

(2) On an electroless plating film, a photosensitive dry film is made to bond by thermo-compression, and, subsequently a photomask film is stuck, expose, carry out a development with alkali, a solvent, etc., and provide plating resist.

(3) Perform electrolysis plating by making an electroless plating film into a plating bar, and form an electrolysis plating film in a resist agenesis portion. As for thickness of this

electrolysis plating film, 5-20 micrometers is good.

(4) Carry out dissolution removal of the electroless plating film under plating resist in a mixed water solution of sulfuric acid-hydrogen peroxide or solution of persulfate, and solution, such as ferric chloride and a cupric chloride, and form a pad conductor circuit and a viahole, after exfoliating plating resist with alkali or a solvent.

(5) Form a solder resist layer and a solder vamp through process (8) - (12) in a method mentioned above hereafter.

[0053]

[Example]

(Example 1)

(1) Copper clad laminate which the 18-micrometer copper foil 8 comes to laminate to both sides of the substrate 1 which consists of 1-mm-thick glass epoxy resin or BT (bismaleimide triazine) resin was made into the charge of a start material (refer to drawing 1(a)). The inner layer copper pattern 4 was formed in both sides of the substrate 1 by etching the copper foil 8 of this copper clad laminate into pattern state in accordance with a conventional method (refer to drawing 1(b)).

[0054](2) Wash in cold water the substrate which formed the inner layer copper pattern 4 above (1), and after drying, carry out acid degreasing of the substrate, and carry out soft etching and it ranks second, Process with the catalyst solution which consists of a palladium chloride and organic acid, and a Pd catalyst is given, 8 g/l of copper sulfate, nickel sulfate after activating this catalyst 0.6 g/l, 15 g/l of citrate, 29 g/l of sodium hypophosphite, 31 g/l of boric acid, It plates with surface-active agent 0.1g/l and the nonelectrolytic plating bath which consists of pH=9, and is the thickness of a Cu-nickel-P alloy to all the surfaces of the copper conductor circuit 3. A 2.5-micrometer roughened layer (uneven layer) was formed (however, this roughened layer is not shown). And further, wash the substrate in cold water and it is immersed in the unelectrolyzed tin substitution plating bath which consists of 0.1 mol/l Howe fluoridation - 1.0 mol/l thiourea liquid at 50 degrees C for 1 hour, It is thickness to the surface of said Cu-nickel-P alloy roughened layer. A 0.3-micrometer tin substitution plating layer was formed (however, not shown [this tin substitution plating layer]).

[0055](3) the cresol novolak type epoxy resin (the Nippon Kayaku make.) which dissolved in DMDG (diethylene glycol dimethyl ether) The acrylic ghost of the molecular weight 2500 25% 70 weight sections, polyether sulphone (PES) 30 weight section, Imidazole hardening agent (made in [Shikoku Chemicals], trade name:2E4 MZ-CN) 4 weight section, caprolactone conversion tris (AKUROKISHI ethyl) isocyanurate (the Toagosei make.) which is a photosensitive monomer Trade name : ARONIKKUSU M325 10 weight section, benzophenone (made by Kanto Kagaku) 5 weight section as a photoinitiator, the Michler's-ketone (made by Kanto Kagaku) 0.5 weight section as a photosensitizer -- receiving this mixture further -- mean particle diameter [] of an epoxy resin particle -- a 5.5-micrometer thing 35 weight sections, Mean particle diameter After mixing five weight sections for a 0.5-micrometer thing, it mixed adding NMP (normal methyl pyrrolidone), it adjusted and kneaded to the viscosity of 12 Pa, and s with 3 rolls continuously the HOMODI spar agitator, and the photosensitive adhesives solution (resin insulation between layers) was obtained.

[0056](4) After using and applying the roll coater to both sides of the substrate which finished processing of the above (2) for the photosensitive adhesives solution obtained

above (3) and neglecting it to them for 20 minutes by the horizontal state, desiccation for 30 minutes was carried out to them at 60 degrees C, and the 60-micrometer-thick adhesives layer 2 was formed in them.

[0057](5) The photomask film in which the viahole was drawn was laid in both sides of the substrate which formed the adhesives layer 2 above (4), and ultraviolet rays were irradiated with and exposed.

(6) By carrying out spray development of the exposed substrate with a DMTG (triethylene glycol wood ether) solution, the opening used as the viahole of 2 100 micrometers of adhesives layers phi was formed. The substrate concerned is exposed by 3000mJ/cm² with an ultrahigh pressure mercury lamp, and it is 1 hour and after that at 100 degrees C. by heat-treating at 150 degrees C in 5 hours, The adhesives layer 2 with a thickness of 50 micrometers which has the opening (opening 6 for viahole formation) excellent in the dimensional accuracy equivalent to a photomask film was formed. A tinning layer is selectively exposed to the opening 6 used as a viahole.

[0058](7) Above (5). The substrate which formed the opening 6 for viahole formation by (6) is immersed in chromic acid for 2 minutes, dissolution removal of the epoxy resin particle which exists in the adhesives layer 2 surface is carried out, and the surface of the adhesives layer concerned is roughened.

Then, after being immersed in the neutralized solution (made by SHIPUREI), it washed in cold water (refer to drawing 1 (c)).

[0059](8) The catalyst core was given to the surface of the adhesives layer 2 and the opening 6 for viaholes by giving a palladium catalyst (product made from ATOTEKKU) to the substrate which performed the surface roughening process (a roughening depth of 20 micrometers) above (7).

[0060]Oligomer (molecular weight 4000) of the photosensitive grant which acrylic-ized 50% of the epoxy group of 60% of the weight of the cresol novolak type epoxy resin (made by Nippon Kayaku) in which DMDG was dissolved (9) 46.67 g, 80% of the weight of the bisphenol A type epoxy resin (the product made from oil recovery shell.) in which methyl ethyl ketone was dissolved Epicoat 1001 15.0g and an imidazole hardening agent (made in Shikoku Chemicals.) Trade name: Similarly multivalent acrylic monomer (product made from Kyoeisha chemicals and trade name:DPE6A) 1.5 g was mixed, and 2E4 MZ-CN1.6 g and 3 g of multivalent acrylic monomers (Nippon Kayaku make and trade name:R604) which are photosensitive monomers prepared the mixed liquor A. On the other hand, it was made to dissolve in 3-g DMDG which warmed Michler's-ketone (made by Kanto Kagaku) 0.2 g as 2 g of benzophenone (made by Kanto Kagaku) as a photoinitiator, and a photosensitizer at 40 degrees C, and the mixed liquor B was prepared. Mixed stirring of the above-mentioned mixed liquor A and the above-mentioned mixed liquor B was carried out, and the liquid resist constituent was obtained.

[0061](10) The above-mentioned liquid resist constituent was used for both sides of the substrate which finished processing of catalyst core grant above (8), the roll coater was applied to them, desiccation for 30 minutes was carried out to them at 60 degrees C, and the 30-micrometer-thick regist layer was formed in them.

[0062](11) The mask in which the pattern was drawn by said regist layer was laminated, and ultraviolet rays were irradiated with and exposed.

(12) After exposing above (11), dissolution development of the regist layer was carried out by DMTG, the plating resist 3 from which the conductor circuit pattern part escaped was

formed on the substrate, and this was further exposed by $6000\text{mJ}/\text{cm}^2$ with the ultrahigh pressure mercury lamp. And let this plating resist 3 be the permanent resist 3 formed on said adhesives layer 2 further by heat-treating at 150 degrees C after that by 100 degrees C in 3 hours for 1 hour.

[0063](13) Perform plating pretreatment (specifically activation of a catalyst core, such as vitriolization) to the substrate in which the permanent resist 3 was formed, beforehand. Then, the conductor layer by an additive process was formed by performing copper plating by an electrolytic copper plating bath, depositing non-electrolytic copper plating about 15 micrometers thick in a resist agenesis part, and forming the outer layer copper pattern 5 and the viahole 7 (refer to drawing 1 (d)).

(14) Subsequently, they are 8 g/l of copper sulfate, and nickel sulfate about the substrate in which the conductor layer was formed. 0.6 g/l, 15 g/l of citrate, 29 g/l of sodium hypophosphite, 31 g/l of boric acid, surface-active agent It was immersed in the electroless plating liquid of pH=9 which consists of 0.1 g/l, and the roughened layer 11 which consists of copper-nickel phosphorus was formed in the surface of this conductor layer (refer to drawing 1 (e)).

[0064](15) Oligomer (molecular weight 4000) of the photosensitive grant which, on the other hand, acrylic-ized 50% of the epoxy group of 60% of the weight of the cresol novolak type epoxy resin (made by Nippon Kayaku) dissolved in DMDG 46.67 g, 80% of the weight of the bisphenol A type epoxy resin (the product made from oil recovery shell.) in which methyl ethyl ketone was dissolved Epicoat 1001 15.0g and an imidazole hardening agent (made in Shikoku Chemicals.) trade name: -- the multivalent acrylic monomer (the Nippon Kayaku make.) which are 2E4 MZ-CN1.6 g and a photosensitive monomer trade name: -- R6043g -- the same -- a multivalent acrylic monomer (the product made from the Kyoeisha chemicals.) Trade name : Six A1.5 g of DPEs and 0.71 g of dispersed system defoaming agents (the Sannopuko make, trade name:S-65) are mixed, The soldering resist composition which furthermore adjusted [the benzophenone (made by Kanto Kagaku) as a photoinitiator] 0.2 g, in addition viscosity for the Michler's ketone (made by Kanto Kagaku) as 2 g and a photosensitizer to 2.0 Pa-s at 25 degrees C to this mixture was obtained. In the case of 60 rpm, in the case of rotor No.4 and 6 rpm, measurement of viscosity was based on rotor No.3 by the Brookfield viscometer (Tokyo Keiki and DVL-B type).

[0065]It inserted between the rolls 19 for spreading of the couple of the roll coater 18 shown in drawing 2 where the substrate obtained at the process to (16) and (14) is stood vertically, and the soldering resist composition obtained above (15) on the surface of this substrate was applied twice, and the 20-micrometer-thick resin layer was formed. Here, in the 1st spreading, 75 degrees C and desiccation for 20 minutes were performed, and 75 ** and desiccation for 30 minutes were performed in the 2nd spreading.

(17) After ranking second and forming a resin layer in the surface of said substrate, the DMTG development of this resin layer was exposed and carried out by the ultraviolet rays of $1000\text{mJ}/\text{cm}^2$. At 80 degrees C, it heat-treated at 120 degrees C by 100 degrees C for 1 hour for 1 hour, and heat-treated on the conditions of 3 hours by 150 degrees C for 1 hour, and the solder resist layer (opening diameter 200 micrometers) (20 micrometers in thickness) 14 in which the pad portion carried out the opening was formed (refer to drawing 1 (f)).

[0066]The substrate in which the solder resist layer 14 was formed (18) Next, 30 g/l of

nickel chloride, It was immersed in the electroless nickel plating liquid of pH=5.5 which consists of 10 g/l of sodium hypophosphite, 10 g/l of sodium acid citrate, 20 g/l of glycines, and lead nitrate 2 mg/l for 30 minutes, and the 4-micrometer-thick nickel plating layer 15 was formed in the opening. The substrate 2 g/l of gold cyanide potassium, 75 g/l of ammonium chloride, It was immersed in the unelectrolyzed gold plating liquid of pH=5 which consists of 50 g/l of sodium acid citrate, and 10 g/l of sodium hypophosphite for 30 minutes on 90 degrees C conditions, and the 0.05-micrometer-thick gold plating layer 16 was formed on the nickel plating layer 15 (refer to drawing 1 (g)).

(19) and soldering paste is printed to the opening of the solder resist layer 14 (a solder replica method may be used) -- by carrying out a reflow at 200 degrees C, the solder vamp 17 was formed and the printed wired board which has the solder vamp 17 was manufactured (refer to drawing 1 (h)).

[0067](Comparative example 1) making it be the same as that of Example 1 except having used what adjusted DMDG to the constituent of Example 1 (15), and adjusted 14g, in addition viscosity to 0.2 Pa-s as a soldering resist composition -- (16) -- until -- it processed. However, the above-mentioned soldering resist composition had too low [to be easy to be hung down] viscosity, was not able to be changed into the state where the wiring board was stood vertically, and was not able to be applied to double-sided coincidence. Then, the wiring board was leveled, the above-mentioned soldering resist composition was applied by the curtain coat method, and the printed wired board which has a solder vamp like Example 1 was manufactured.

[0068](Comparative example 2) In Example 1 (15), the printed wired board which has a solder vamp was manufactured like Example 1 except having obtained the soldering resist composition which adjusted viscosity to 15 Pa-s using the cresolnovolak type epoxy acrylate of solid content 70%. In this comparative example 2, since the viscosity of a soldering resist composition was too high, unevenness occurred on the surface of the solder resist layer.

[0069](Comparative example 3) the constituent (polyglycidyl ether of o-cresol-form aldehyde novolac.) of the experimental run number 1-1 given [as a soldering resist composition] in JP,63-286841,A Processing to (16) was carried out like Example 1 except having used the soldering resist composition of viscosity 0.2 Pa and, and s containing a cellosolve acetate, benzophenone, and a Michler's ketone. However, the above-mentioned soldering resist composition had too low [to be easy to be hung down] viscosity, was not able to be changed into the state where the wiring board was stood vertically, and was not able to be applied to double-sided coincidence. Then, according to JP,63-286841,A, by the curtain coat method, the above-mentioned solder resist was applied on the surface of the wiring board, and the printed wired board which has a solder vamp like the above-mentioned Example 1 was manufactured after that.

[0070](Comparative example 4) As a soldering resist composition, the constituent of the statement was used for JP,62-23036,A, and the printed wired board which has a solder vamp like Example 1 was manufactured except having made the development of the solder resist layer into alkaline development.

[0071]Thus, about the manufactured printed wired board, the spreading nature of the soldering resist composition was checked, and the HAST test (High Acceleration Stress Test) was carried out, and the short existence between solder vamps after an examination was measured by the checker. HAST test conditions are 85% of humidity, and temperature.

They could be 135 degrees C, and impressed-electromotive-force 3.3 V or 48 hours. The existence of the halo phenomenon by viewing was checked, further, 1000 heat cycle tests were carried out by -55 - 125 degrees C, and the existence of exfoliation of a solder resist layer was checked with the optical microscope. These results are shown in Table 1.

[0072]When changing into the state where the wiring board was stood, in Example 1 which is an example of this invention and applying a soldering resist composition by a roll coater, the spreading nature was good. On the other hand, in the comparative example 1 which is too low, or the comparative example 2 the viscosity is too high, the spreading nature of the soldering resist composition was bad. Leaden migration was not checked in Example 1, but there was no generating with a poor short circuit after the HAST test resulting from the existence of this migration. On the other hand, in the comparative examples 2 and 4, since the viscosity was low even if it was using the soldering resist composition of the same presentation as Example 1, leaden migration was checked and the short defect occurred after the HAST test. Furthermore, in Example 1, since the glycol ether system solvent was used, a conductor circuit was not oxidized and exfoliation of the solder resist layer by the halo phenomenon or a thermo cycle was not observed. On the other hand, in the comparative example 3 which is using the cellosolve acetate, exfoliation by the halo phenomenon or a thermo cycle was observed.

[0073]

[Table 1]

	塗布性	H A S T試験	ハロー現象	ヒートサイクル試験
実施例 1	良	ショート無し	無	剥離無し
実施例 2	良	ショート無し	無	剥離無し
比較例 1	不可	ショート有り	無	剥離無し
比較例 2	表面凹凸	ショート無し	無	剥離無し
比較例 3	不可	ショート有り	有	剥離有り
比較例 4	良	ショート有り	無	剥離無し

[0074](Example 2)

A. -- preparation . cresol novolak type epoxy resin (the Nippon Kayaku make.) of the adhesive composition for nonelectrolytic plating They are 35 weight sections, photosensitive monomer (Toagosei make, ARONIKKUSU M315) 3.15 weight section, defoaming agent (Sannopuko make, S-65) 0.5 weight section, and NMP about the resin liquid in which DMDG was made to dissolve the 25% acrylic ghost of the molecular weight 2500 by 80wt% of concentration 3.6 Stirring mixing of the weight section was carried out.

polyether sulphone (PES) 12 weight section and an epoxy resin particle (Mitsuhiro -- transformation -- make.) Mean particle diameter of a polymer pole After mixing [a 1.0-micrometer thing] 3.09 weight sections for 7.2 weight section and a thing with a mean particle diameter of 0.5 micrometer, NMP30 weight section was added further and stirring mixing was carried out by the bead mill.

The amount part of imidazole hardening agent (made in [Shikoku Chemicals], 2E4 MZ-CN) duplexs, the amount part of photoinitiator (Ciba-Geigy make, IRGACURE I-907) duplexs, photosensitizer (Nippon Kayaku make, DETX-S) 0.2 weight section, and NMP1.5 Stirring mixing of the weight section was carried out.

These were mixed and the adhesive composition for nonelectrolytic plating was prepared. [0075]B. preparation. cresol novolak type epoxy resin (the Nippon Kayaku make.) of the lower layer resin insulating agent between layers They are 35 weight sections, photosensitive monomer (Toagosei make, ARONIKKUSU M315) 4 weight section, defoaming agent (Sannopuko make, S-65) 0.5 weight section, and NMP about the resin liquid in which DMDG was made to dissolve the 25% acrylic ghost of the molecular weight 2500 by 80wt% of concentration 3.6 Stirring mixing of the weight section was carried out.

Polyether sulphone (PES) 12 weight section, mean particle diameter of an epoxy resin particle (Mitsuhiro transformation make, a polymer pole) After mixing 14.49 weight section for a 0.5-micrometer thing, NMP30 weight section was added further and stirring mixing was carried out by the bead mill.

The amount part of imidazole hardening agent (made in [Shikoku Chemicals], 2E4 MZ-CN) duplexs, the amount part of photoinitiator (Ciba-Geigy make, IRGACURE I-907) duplexs, photosensitizer (Nippon Kayaku make, DETX-S) 0.2 weight section, and NMP1.5 Stirring mixing of the weight section was carried out.

These were mixed and the resin composition used as an insulating agent layer by the side of the lower layer which constitutes the resin insulating layer between layers of two-layer structure was prepared.

[0076]C. the preparation. bisphenol female mold epoxy monomer (the product made from oil recovery shell.) of a resin filler Mean particle diameter with which the molecular weight 310, 983UYL100 weight section, and the surface were coated with the silane coupling agent SiO₂ spherical particle which is 1.6 micrometers (the product made from an ADOMA tech, CRS 1101-CE, and here) below the thickness (15 micrometers) of the inner layer copper pattern mentioned later carries out the size of grain of maximum size -- 170 weight sections and leveling agent (Sannopuko make, PERENORU S4) 1.5 weight section were kneaded with 3 rolls, and the viscosity of the mixture was adjusted to 45,000-49,000 cps at 23 ± 1 degrees C.

Imidazole hardening agent (made in [Shikoku Chemicals], 2E4 MZ-CN) 6.5 weight section.

These were mixed and the resin filler 10 was prepared.

[0077]D. 2-ethylhexyl acrylate and butyl acrylate were mixed at a rate of 53:47 by the weight ratio in the example of manufacture 1 xylene solvent of an acrylic ester polymer, it heated at 50 degrees C, using dimethylaniline (tertiary amine) as an initiator, and copolymerization was carried out with the conventional method. Ethyl acrylate and hydroxyethyl acrylate were polymerized independently in a similar manner, respectively. The copolymer of 2-ethylhexyl acrylate and butyl acrylate, The polymer of ethyl acrylate and the polymer of hydroxyethyl acrylate were mixed, respectively so that it might be set to 2-ethylhexyl acrylate:butyl acrylate:ethyl acrylate:hydroxyethyl acrylate =49:42:6:3 by a weight ratio, and heating removal of the xylene was carried out. Although the obtained constituent tried the reprecipitation to methanol, polymer does not sediment but it is presumed that a molecular weight is about 2000 to about 3000. About the obtained

constituent, FT-IR spectrum, ^1H -NMR, and ^{13}C -NMR were measured. The result is shown in drawing 25, drawing 26, and drawing 27. It was proved from the data of such IR and NMR that a compound was a polymer of acrylic ester.

[0078][A measuring device and a measuring condition]

FT-IR device: -- PerkinElmer 1650 measuring method: -- a penetration method (KRS-5)

NMR device : JEOL EX-400

Chemical-shift standard: CDCl_3 ; ^1H 7.25ppm and a ^{13}C 77.05ppm sample were dissolved in heavy chloroform, five drops of pyridine- d_5 was added, and it measured at the room temperature.

[0079]E. Copper clad laminate which the 18-micrometer copper foil 8 laminates to both sides of the substrate 1 which consists of glass epoxy resin with a manufacturing method (1) thickness of 1 mm or BT (bismaleimide triazine) resin of a printed wired board was made into the charge of a start material (refer to drawing 4). First, after carrying out drill drilling of this copper clad laminate and forming plating resist, the inner layer copper pattern 4 was formed in both sides of the substrate 1 by carrying out nonelectrolytic plating processing, forming the through hole 9, and etching the copper foil 8 into pattern state in accordance with a conventional method further.

[0080](2) Wash in cold water the substrate in which the inner layer copper pattern 4 and the through hole 9 were formed, and after drying, as an oxidation bath (melanism bath), By oxidation-reduction processing using NaOH (10 g/l) and NaBH_4 (6 g/l) as NaOH (10 g/l), NaClO_2 (40 g/l), Na_3PO_4 (6 g/l), and a reduction bath. The roughened layer 11 was formed in the surface of the inner layer copper pattern 4 and the through hole 9 (refer to drawing 5).

[0081](3) The resin filler 10 by using and applying a roll coater to one side of a substrate, It is filled up between the conductor circuits 4 or in the through hole 9, and is made to dry in 70 degrees C and 20 minutes, and about the field of another side, similarly, it was filled up with the resin filler 10 between the conductor circuits 4 or in the through hole 9, and stoving was carried out in 70 degrees C and 20 minutes (refer to drawing 6).

[0082](4) One side of a substrate which finished processing of the above (3) by belt sander polish using the belt abrasive paper (made by Sankyo Rikagaku) of #600. It ground so that the resin filler 10 might remain in neither the surface of the inner layer copper pattern 4, nor the land surface of the through hole 9, and it ranked second, and buffing for removing the crack by said belt sander polish was performed. Such a series of polishes were similarly performed about the field of another side of a substrate. Subsequently, it carried out at 150 degrees C for 1 hour for 3 hours, 100 degrees C performed heat-treatment of 7 hours at 180 degrees C at 120 degrees C for 1 hour, and the resin filler 10 was hardened (refer to drawing 7).

[0083]Thus, remove the roughened layer 11 of the layer part of the resin filler 10, and the inner layer conductor circuit 4 upper surface with which the through hole 9 grade was filled up, and substrate both sides are smoothed, The wiring board which the resin filler 10 and the side of the inner layer conductor circuit 4 stuck firmly via the roughened layer 11, and the internal surface and the resin filler 10 of the through hole 9 stuck firmly via the roughened layer 11 was obtained. That is, the surface of the resin filler 10 and the surface of the inner layer copper pattern 4 turn into the same flat surface by this process. Tg point

of filled hardening resin was [here,] 155.6 degrees C, and the line coefficient of thermal expansion was 44.5×10^{-6} /degrees C.

[0084](5) It is thickness to the land upper surface of the inner layer conductor circuit 4 and the through hole 9 exposed by processing of the above (4). The roughened layer (uneven layer) 11 which consists of a 2.5-micrometer Cu-nickel-P alloy is formed, It is thickness to the surface of the roughened layer 11. A 0.3-micrometer Sn layer was provided (not shown about refer to [drawing 8](#), however a Sn layer). The formation method is as follows.

Namely, carry out acid degreasing, and carry out soft etching, and rank second and a substrate is processed with the catalyst solution which consists of a palladium chloride and organic acid, 8 g/l of copper sulfate, nickel sulfate after giving a Pd catalyst and activating this catalyst 0.6 g/l, 15 g/l of citrate, 29 g/l of sodium hypophosphite, 31 g/l of boric acid, surface-active agent It plated with 0.1 g/l and the nonelectrolytic plating bath which consists of pH=9, and the roughened layer 11 of the Cu-nickel-P alloy was formed in the copper conductor circuit 4 upper surface and the land upper surface of the through hole 9. this substrate is received -- heat-treatment of 2 hours being performed [100 degrees C] during 30 minutes and at 150 degrees C for 30 minutes and by 120 degrees C, and it processing in sulfuric acid solution and the Howe fluoric acid solution of 0.2 mol/l 10% of the weight, and subsequently, The Cu-Sn substitution reaction was carried out on condition of Howe 0.1 mol/l. stannous-fluoride, thiourea 1.0 mol/l, temperature [of 50 degrees C], and pH=1.2, and the Sn layer of thickness 0.3 mum was provided in the surface of the roughened layer 11 (not shown about a Sn layer).

[0085](6) To both sides of the substrate of the above (5), it is a resin insulating agent between layers of B (viscosity 1.5 Pa-s). After applying by the roll coater and neglecting it for 20 minutes by the horizontal state, desiccation for 30 minutes (prebaking) was performed at 60 degrees C, and the insulating agent layer 2a was formed. After using the roll coater, applying the adhesives for nonelectrolytic plating of A (viscosity 7 Pa-s) on this insulating agent layer 2a furthermore and neglecting it for 20 minutes by a horizontal state, desiccation for 30 minutes (prebaking) was performed at 60 degrees C, and adhesives layer 2b was formed (refer to [drawing 9](#)).

[0086](7) The photomask film in which the black spot of 85 micrometerphi was printed was stuck to both sides of the substrate which formed the insulating agent layer 2a and adhesives layer 2b above (6), and it exposed by 500 mJ/cm^2 with the ultrahigh pressure mercury lamp. Spray development of this is carried out with a DMTG solution, the substrate concerned is further exposed by 3000 mJ/cm^2 with an ultrahigh pressure mercury lamp, and it is 1 hour and after that at 100 degrees C. by carrying out heat-treatment (postbake) of 5 hours at 150 degrees C, The resin insulating layer 2 with a thickness of 35 micrometers which has an opening (opening 6 for viahole formation) of 85 micrometerphi excellent in the dimensional accuracy equivalent to a photomask film between layers (two-layer structure) was formed (refer to [drawing 10](#)). The tinning layer was selectively exposed to the opening used as a viahole.

[0087](8) By immersing the substrate with which the opening was formed for 19 minutes at 70 degrees C in chromic acid of 800 g/l, and carrying out dissolution removal of the epoxy resin particle which exists in the surface of adhesives layer 2b of the resin insulating layer 2 between layers, The surface of the resin insulating layer 2 between the layers concerned was made into the split face (a depth of 3 micrometers), and after being immersed in the neutralized solution (made by SHIPUREI) after that, it washed in cold

water (refer to drawing 11). The catalyst core was attached to the surface of the resin insulating layer 2 between layers, and the internal surface of the opening 6 for viaholes by giving a palladium catalyst (product made from ATOTEKKU) to the surface of this substrate that carried out the surface roughening process.

[0088](9) The substrate was immersed during the non-electrolytic copper plating bath of the following presentations, and the non-electrolytic copper plating film 12 of thickness 0.6 μm was formed in the whole split face (refer to drawing 12). Heat-treatment of 2 hours was performed [100 degrees C] for 30 minutes and at 150 degrees C during 30 minutes and by 120 degrees C at 50 degrees C to this electroless plating film for 1 hour.

[Electroless plating liquid]

EDTA 150 g/l copper sulfate 20 g/lHCHO 30 ml/lNaOH 40 g/lalpha and alpha'-bipyridyl 80 mg/lPEG 0.1 g/l [Nonelectrolytic plating conditions]

It is 70 degrees C in the degree of solution temperature, and is 30 minutes. [0089](10) On the non-electrolytic copper plating film 12 formed above (9), the commercial photosensitive dry film was stuck, the mask was laid, the development was carried out by exposure and 0.8 % sodium carbonate by 100 mJ/cm^2 , and the 15-micrometer-thick plating resist 3 was formed (refer to drawing 13).

[0090](11) Subsequently, after processing the electroless plating film surface in sulfuric acid solution 10%, electrolytic copper plating was performed to the resist agenesis portion on condition of the following, and the 15-micrometer-thick electrolytic copper plating film 13 was formed (refer to drawing 14). To this electrolysis plating film, it gave for 30 minutes at 80 degrees C for 30 minutes, and heat-treatment of 5 hours was performed [50 degrees C] for 30 minutes and at 150 degrees C for 30 minutes and by 120 degrees C at 100 degrees C.

[Electrolysis plating liquid]

Sulfuric acid 180 g/l copper sulfate 80 g/l additive agent (made in [ATOTEKKU Japan], KAPARASHIDO GL) 1 ml/l [Electrolysis plating conditions]

Current density 1A/ dm^2 time 30-minute temperature Room temperature [0091](12) After carrying out the strip of the plating resist 3 by KOH 5%, a surface treatment is carried out in sulfuric acid solution 10%, Furthermore, the etching process of the electroless plating film 12 under the plating resist 3 was carried out with the mixed liquor of sulfuric acid and hydrogen peroxide, dissolution removal was carried out and the conductor circuit (a viahole is included) 5 with a thickness of 18 micrometers which consists of the non-electrolytic copper plating film 12 and the electrolytic copper plating film 13 was formed. It was immersed in 800 g/l of chromic acid for 3 minutes at 70 degrees C, the 1-2-micrometer etching process of the surface of the adhesives layer for nonelectrolytic plating between the conductor circuits located in a conductor circuit agenesis portion was carried out, and the palladium catalyst which remains on the surface was removed (refer to drawing 15).

[0092](13) About the substrate in which the conductor circuit 5 was formed, they are 8 g/l of copper sulfate, and nickel sulfate. 0.6 g/l, 15 g/l of citrate, 29 g/l of sodium hypophosphite, 31 g/l of boric acid, surface-active agent It was immersed in the electroless plating liquid of pH=9 which consists of 0.1 g/l, and the roughened layer 11 which consists of 3-micrometer-thick copper-nickel phosphorus was formed in the surface of this conductor circuit 5 (refer to drawing 16). It is Cu when the formed roughened layer 11 was analyzed by EPMA (X-ray fluorescence device) at this time. : 98-mol%, nickel : 1.5 mol%,

P: It was 0.5-mol% of composition ratio. The Cu-Sn substitution reaction was performed on condition of Howe stannous-fluoride 0.1 mol/l, thiourea 1.0 mol/l, temperature [of 50 degrees C], and pH=1.2, and the 0.3-micrometer-thick Sn layer was provided in the surface of said roughened layer 11 (not shown about a Sn layer).

[0093](14) The aforementioned (6) By repeating the process of - (13), the upper conductor circuit was formed further and the multilayer printed wiring board was obtained. However, Sn substitution was not performed (drawing 17 - 22 references).

[0094](15) Oligomer (molecular weight 4000) 46.67 weight section of the photosensitive grant which, on the other hand, acrylic-ized 50% of the epoxy group of cresol novolak type epoxy resin (made by Nippon Kayaku), Bisphenol A type epoxy resin (product made from oil recovery shell, Epicoat 1001) 14.121 weight section, Imidazole hardening agent (made in [Shikoku Chemicals], 2E4 MZ-CN) 1.6 Weight section, The multivalent acrylic monomer (Nippon Kayaku make, R604) 1.5 weight section which is a photosensitive monomer, Similarly Multivalent acrylic monomer (product made from Kyoeisha chemicals, DPE6A) 3.0 weight section, Acrylic ester polymer 0.36 compounded by D A weight section is mixed, It is IRGACURE I907 2.0 (made by Ciba-Geigy) as a photoinitiator to these mixtures. Weight section, The DETX-S(made by Nippon Kayaku) 0.2 weight section was added as a photosensitizer, DMDG(diethylene glycol dimethyl ether)1.0 weight section was added further, and the soldering resist composition which adjusted viscosity to 1.4 ± 0.3 Pa and s at 25 degrees C was obtained. In the case of 60 rpm, in the case of rotor No.4 and 6 rpm, measurement of viscosity was based on rotor No.3 by the Brookfield viscometer (Tokyo Keiki and DVL-B type).

[0095](16) The above-mentioned soldering resist composition was applied to both sides of the multilayer interconnection board obtained above (14) by a thickness of 20 micrometers. Subsequently, after carrying out for 20 minutes at 70 degrees C and performing the drying process for 30 minutes at 70 degrees C, the photomask film which is 5 mm in thickness by which the circle pattern (mask pattern) was drawn was stuck, it laid, and the DMTG development was exposed and carried out by the ultraviolet rays of $1000\text{mJ}/\text{cm}^2$. And further, by 80 degrees C, it heat-treated at 120 degrees C by 100 degrees C for 1 hour for 1 hour, and heat-treated on the conditions of 3 hours at 150 degrees C for 1 hour, and the solder resist layer (opening diameter 200 micrometers) (20 micrometers in thickness) 14 which carried out the opening of the solder pad portion (a viahole and its land part are included) was formed.

[0096](17) Next, the substrate in which the solder resist layer 14 was formed is immersed in the electroless nickel plating liquid of pH=5 which consists of 30 g/l of nickel chloride, 10 g/l of sodium hypophosphite, and 10 g/l of sodium acid citrate for 20 minutes, The 5-micrometer-thick nickel plating layer 15 was formed in the opening. The substrate is immersed in the unelectrolyzed gold plating liquid which consists of 2 g/l of gold cyanide potassium, 75 g/l of ammonium chloride, 50 g/l of sodium acid citrate, and 10 g/l of sodium hypophosphite for 23 seconds on 93 degrees C conditions, The 0.03-micrometer-thick gold plating layer 16 was formed on the nickel plating layer 15.

[0097](18) And by printing soldering paste to the opening of the solder resist layer 14, and carrying out a reflow to it at 200 degrees C, the solder vamp (solder object) 17 was formed and the printed wired board which has the solder vamp 17 was manufactured (refer to drawing 23).

[0098]Thus, about the manufactured printed wired board, the check of the check of

spreading nature, a HAST test, and a halo phenomenon and the heat cycle test were done like Example 1 and the comparative example. The result is combined with Table 1 and shown. The existence of air bubbles was investigated about the solder resist layer of Example 1 and Example 2 using the optical microscope. As a result, although survival of air bubbles was seen in the solder resist layer of Example 1, in the solder resist layer of Example 2, air bubbles were not seen at all. Although the solder resist layer of Example 1 had devitrified, the solder resist layer of Example 2 has translucency, and development nature was excellent in the direction of the solder resist layer of Example 2.

[0099]

[Effect of the Invention]As explained above, according to the soldering resist composition of this invention, simultaneous spreading to substrate both sides by a roll coater is possible, and there is no leaden migration. So, the printed wired board of this invention does not have exfoliation of the solder resist layer by the halo phenomenon or a thermo cycle, either, in order not to form an oxide film in the contact-pads surface.

[Brief Description of the Drawings]

[Drawing 1]It is a figure showing one manufacturing process of the printed wired board concerning this invention.

[Drawing 2](a) It is a figure showing the application process of the solder resist applying, and (b) is a figure showing the surface structure of the roller for spreading used for the application process.

[Drawing 3]It is a fragmentary sectional view showing the state where the solder object was provided in the printed wired board of this invention, and the gestalt with which all the surfaces of a pad have exposed (a) in the opening of a solder resist layer, and the gestalt with which the partial surface of a pad has exposed (b) in the opening of a solder resist layer are shown.

[Drawing 4]It is a figure showing each manufacturing process of the printed wired board concerning an invention.

[Drawing 5]It is a figure showing each manufacturing process of the printed wired board concerning an invention.

[Drawing 6]It is a figure showing each manufacturing process of the printed wired board concerning an invention.

[Drawing 7]It is a figure showing each manufacturing process of the printed wired board concerning an invention.

[Drawing 8]It is a figure showing each manufacturing process of the printed wired board concerning an invention.

[Drawing 9]It is a figure showing each manufacturing process of the printed wired board concerning an invention.

[Drawing 10]It is a figure showing each manufacturing process of the printed wired board concerning an invention.

[Drawing 11]It is a figure showing each manufacturing process of the printed wired board concerning an invention.

[Drawing 12]It is a figure showing each manufacturing process of the printed wired board concerning an invention.

[Drawing 13]It is a figure showing each manufacturing process of the printed wired board concerning an invention.

[Drawing 14]It is a figure showing each manufacturing process of the printed wired board

concerning an invention.

[Drawing 15]It is a figure showing each manufacturing process of the printed wired board concerning an invention.

[Drawing 16]It is a figure showing each manufacturing process of the printed wired board concerning an invention.

[Drawing 17]It is a figure showing each manufacturing process of the printed wired board concerning an invention.

[Drawing 18]It is a figure showing each manufacturing process of the printed wired board concerning an invention.

[Drawing 19]It is a figure showing each manufacturing process of the printed wired board concerning an invention.

[Drawing 20]It is a figure showing each manufacturing process of the printed wired board concerning an invention.

[Drawing 21]It is a figure showing each manufacturing process of the printed wired board concerning an invention.

[Drawing 22]It is a figure showing each manufacturing process of the printed wired board concerning an invention.

[Drawing 23]It is a figure showing each manufacturing process of the printed wired board concerning an invention.

[Drawing 24]It is other fragmentary sectional views showing the state where the solder object was provided in the printed wired board of this invention, and the gestalt with which all the surfaces of a pad have exposed (a) in the opening of a solder resist layer, and the gestalt with which the partial surface of a pad has exposed (b) in the opening of a solder resist layer are shown.

[Drawing 25]It is a figure showing FT-IR spectrum of the polymer of the acrylic ester compounded in Example 2.

[Drawing 26]It is a figure showing the ^1H -NMR spectrum of the polymer of the acrylic ester compounded in Example 2.

[Drawing 27]It is a figure showing the ^{13}C -NMR spectrum of the polymer of the acrylic ester compounded in Example 2.

[Description of Notations]

1 Substrate

2 The resin insulating layer between layers (adhesives layer for nonelectrolytic plating)

2a insulating agent layer

2b adhesives layer

3 Plating resist (permanent resist)

4 Inner layer conductor circuit (inner layer copper pattern)

5 Outer layer conductor circuit (outer layer copper pattern)

6 The opening for viaholes

7 Viahole (BVH)

8 Copper foil

9 Through hole

10 Filling resin (resin filler)

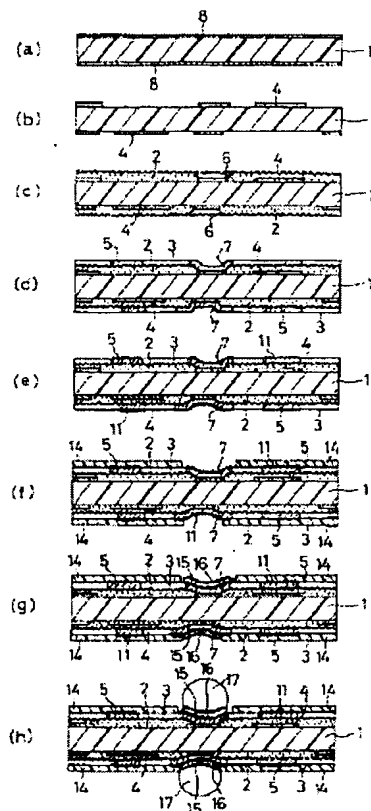
11 Roughened layer

12 Non-electrolytic copper plating film

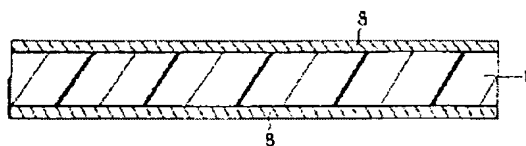
13 Electrolytic copper plating film

- 14 Solder resist layer
- 15 Nickel plating layer
- 16 Gold plating layer
- 17 Solder vamp
- 18 Roll coater
- 19 The roller for spreading
- 20 Doctor bar

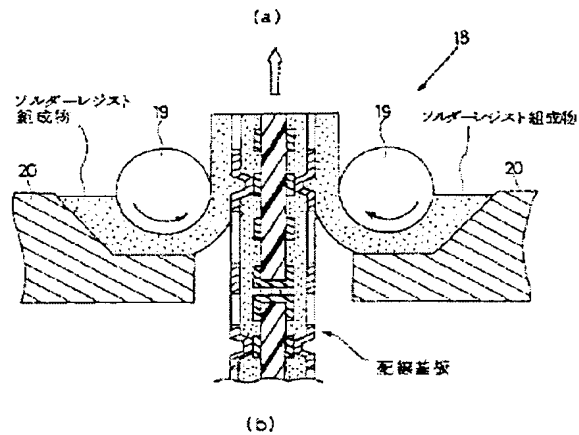
【図1】



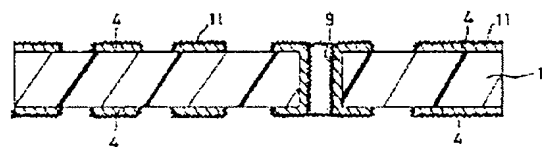
【図4】



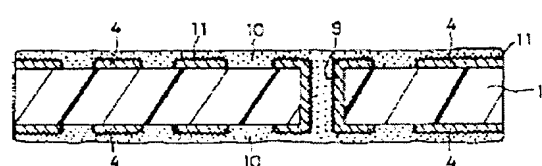
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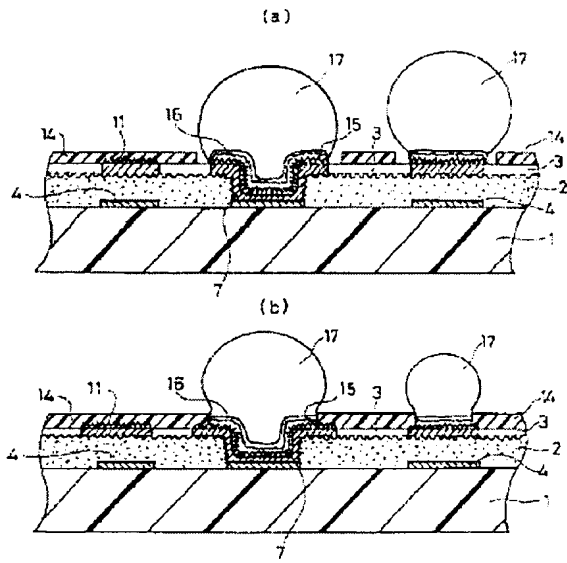
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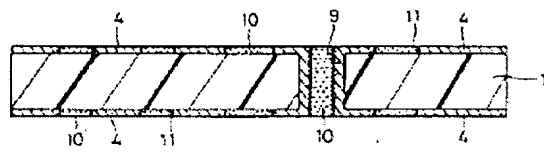
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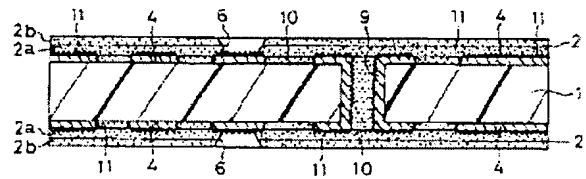
【图 3】



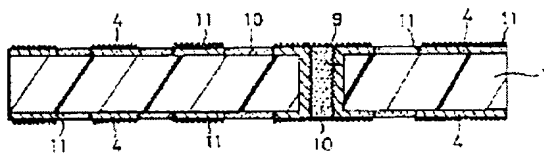
【图 7】



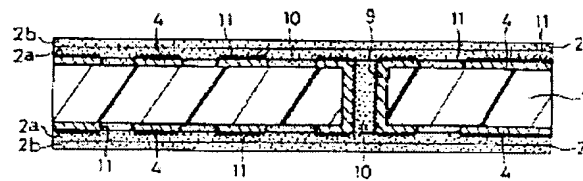
【图 10】



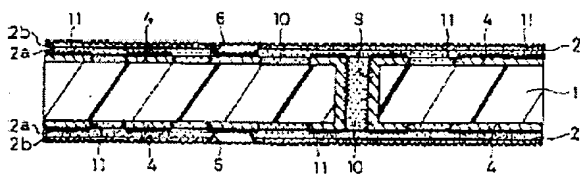
【图 8】



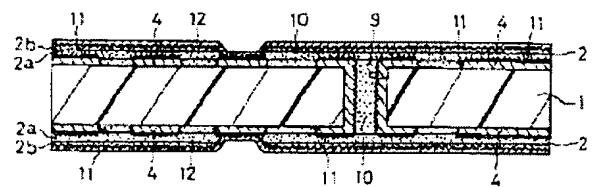
【图 9】



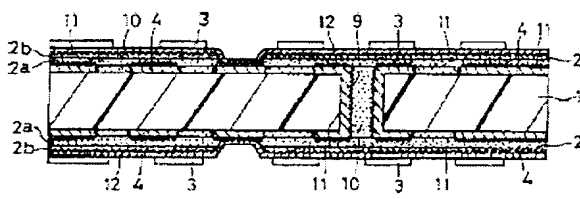
【图 11】



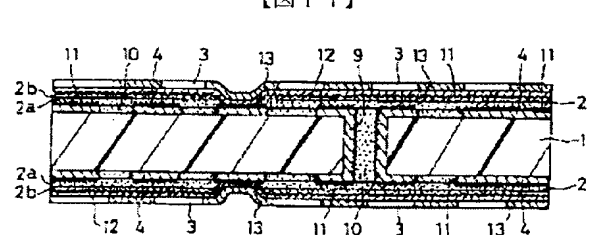
【图 12】



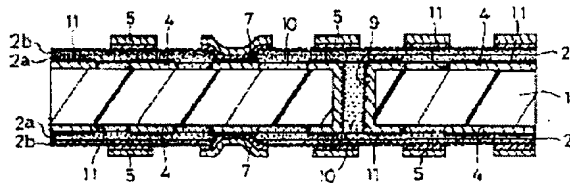
【图 13】



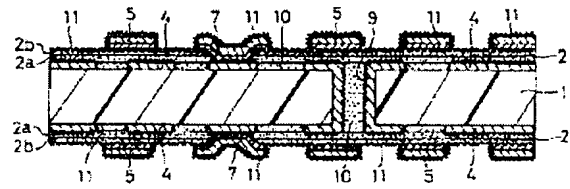
【图 14】



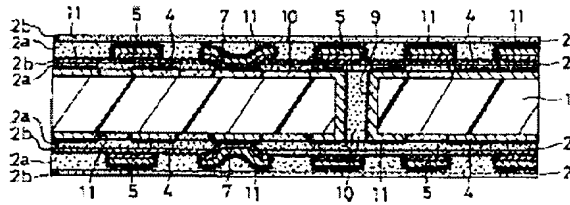
【图 1 5】



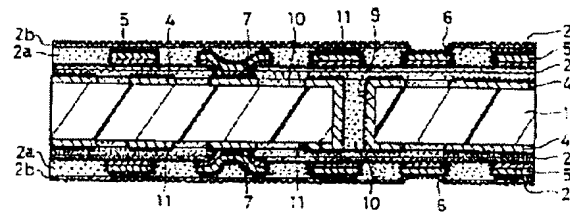
【图 1 6】



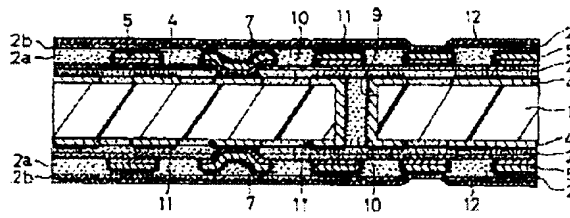
【图 1 7】



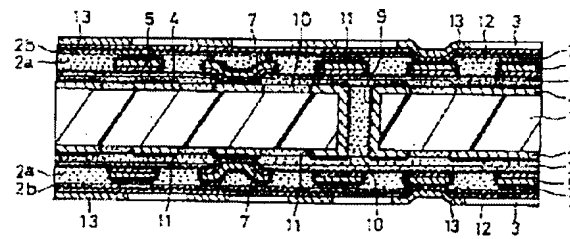
【图 1 8】



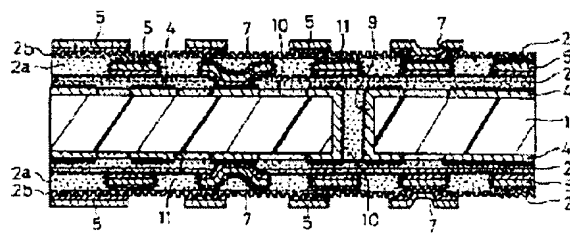
【图 1 9】



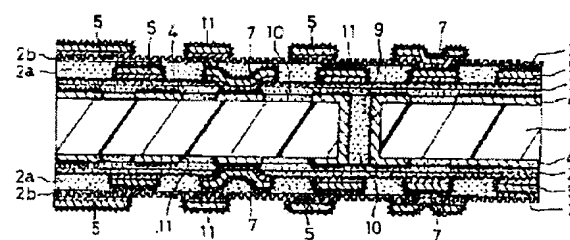
【图 2 0】



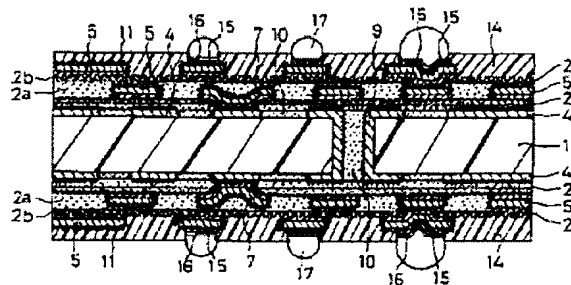
【图 2 1】



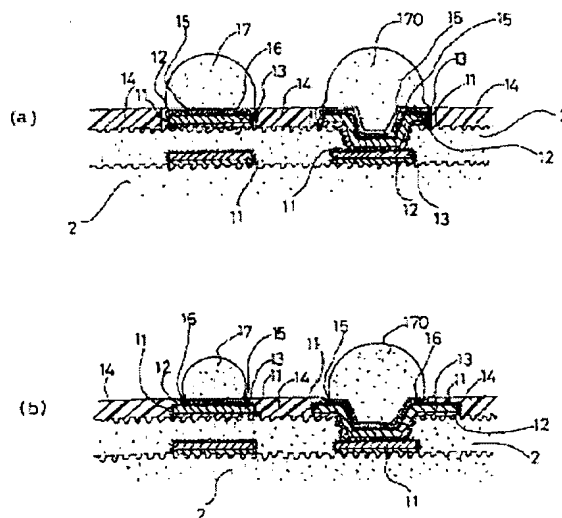
【图 2 2】



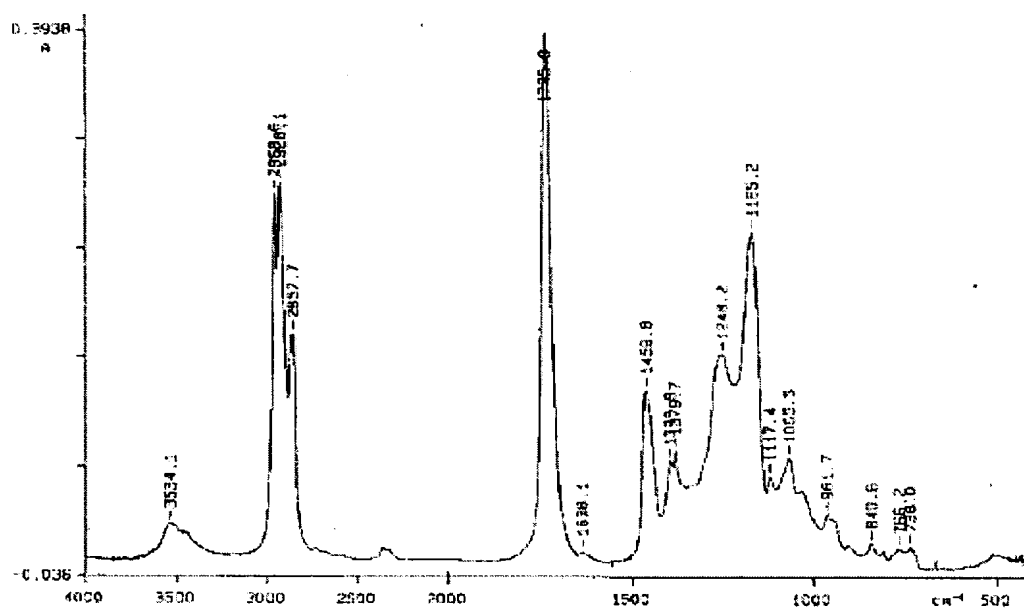
【图 2-3】



【图 2-4】



【图 2-5】



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